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(54) [TITLE OF THE INVENTION] Black silicon nitride quality sinter and method for production thereof

(57) [ABSTRACT]

[Object] This invention relates to a method for the
5 production of a black silicon nitride quality sinter which assumes a black color and exhibits an integral reflectance of not more than 15% to visible ray and ultraviolet light.

[Construction] Silicon nitride and SIALON are stained in a black color to impart to the resultant sinter an integral
10 reflectance of not more than 15% to a visible ray and an ultraviolet light. The staining is effected by a method which comprises causing the sinter to include therein 0.2 - 5 weight % of one species or a plurality of species selected from among TiC, TiCN, NbC, ZrC, HfC, and TaC and adding thereto 0.2 -
15 5 weight % of one species or a plurality of species selected from among V, Cr, Co, Ni, Cu, and Hf as a color tone adjusting agent.

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A black silicon nitride quality sinter,
20 characterized by comprising silicon nitride and not less than 90% of one species or a plurality of species of SIALON and having an integral reflectance of not more than 15% to visible ray and ultraviolet light.

[Claim 2] A black silicon nitride quality sinter according
25 to claim 1, which further comprises 0.2 - 5 wt % of one species or two or more species selected from among TiC, TiC-TiN solid solution, NbC, ZrC, HfC, and TaC as a coloring agent.

[Claim 3] A black silicon nitride quality sinter according
30 to claim 1, which further comprises 0.2 - 5 wt % of one species or a plurality of species from among V, Cr, Fe, Co, Ni, Cu, and Hf in the form of a metal or an oxide as a color tone adjusting agent.

[Claim 4] A black silicon nitride quality sinter according to claim 1, wherein the thermal expansion coefficient of the sinter at a temperature in the range of 20 - 100°C is not more than $2.5 \times 10^{-6}/^{\circ}\text{C}$.

5 [Claim 5] A black silicon nitride quality sinter according to claim 1, wherein the Young's modulus of elasticity is not less than 2.8×10^4 kgf/mm².

[Claim 6] A black silicon nitride quality sinter according to claim 1, wherein the sintering is effected at a temperature
10 in the range of 1600 - 1850°C under application of no pressure or under application of the pressure of atmosphere of nitrogen of not more than 10 kgf/cm².

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

15 [0001]

[Field of Utilization in Industry] This invention relates to a method for the production of a black silicon nitride quality sinter assuming a black color and exhibiting an integral reflectance of not more than 15% to visible ray and
20 ultraviolet light (hereinafter "the integral reflectance exhibited to visible ray and ultraviolet light" will be referred to simply as "reflectance" and the term "integral reflectance" refers to the ratio of the amount of incident light to the total of the amount of light reflected to all
25 the directions).

[0002] A good many of the parts of such optically-related devices as laser-using devices and ultraviolet exposure devices abhor the reflection of light.

[0003] For these parts, materials assuming black color tones
30 and having low degrees of reflectance are required. These parts, when intended to be used in precision devices, are further required to fulfill light weight, high stiffness,

low thermal expansion, and wear resistance.

[0004] The black silicon nitride quality sinter of this invention is an optimum choice for such parts and is widely applied thereto.

5 [0005] Hereinafter, silicon nitride and SIALON are collectively referred to as "a silicon nitride type."

[0006]

[Prior Art] Heretofore, since low reflectance and light weight form a prerequisite for these parts, such parts as
10 are produced by preparing a substrate of an aluminum alloy and treating the surface of this substrate with black alumite have been widely in use.

[0007] Recently, since the precision and the service life required of the machines using these parts have been rigidified,
15 such qualities of aluminum alloys as low stiffness (elasticity), ready plastic deformation, high thermal expansion coefficient, and inferior wear resistance have come to pose a problem.

[0008] While attempts at applying ceramics to these parts
20 have been made therefore, parts thoroughly satisfying black color (low reflectance), high stiffness, light weight, low thermal expansion, and wear resistance are not copiously found in the ceramics.

[0009] JP-A-04-50161 disclosed by us teaches a technique
25 for staining an alumina sinter in a black color.

[0010] The thermal expansion coefficient of alumina, however, is smaller than that of metal but is not sufficiently small. The wear resistance of alumina is not sufficient.

[0011] In contrast thereto, the thermal expansion
30 coefficient of the silicon nitride type is not more than 1/3 of that of alumina and the wear resistance thereof is also excellent. The specific gravity thereof is as light as 80%

of that of alumina. Thus, the silicon nitride type proves excellent where a lighter weight is required.

[0012] The silicon nitride type sinter, however, generally has a light gray color to a gray color. The reflectance thereof is so large as to fall in the range of 20 - 35%.

[0013] As a means to stain this silicon nitride type material, the technique of coloring the material in a golden color type by incorporating in the material about 30% of TiN is available. The reflectance, however, is not appreciably lowered by the golden color type.

[0014] As regards other coloring techniques, JP-A-62-248773 and JP-A-01-192766 have disclosed black silicon nitride quality sinters.

[0015] The former sinter relies on the addition of a compound of Sc, Yb, Er, Ho, or Dy and the latter sinter on the addition of an organic metal compound containing Co or Fe to be stained in a black color. Thus, they differ from this invention.

[0016] JP-A-62-235260 has disclosed a sinter obtained by adding 5 - 40 wt % of at least one species from among TiN, TiC, and Ti(CN) to silicon nitride and subjecting the resultant composition to the HIP treatment. When such an additive is incorporated in such a large amount as mentioned above, however, it brings an increase in the specific gravity of the silicon nitride, impairs the sintering property thereof, requires the HIP and the like to undergo pressure firing, and inevitably raises the price of the produced sinter owing to the expense of this firing.

[0017] The specification of this publication has no mention of the color and the reflectance of the sinter.

[0018]

[Problem to be solved by the invention] None of the known metal materials is found to satisfy high stiffness, low thermal

expansion, light weight, and wear resistance simultaneously.

[0019] As regards ceramics, various materials are known to have reflectances of not more than 15%. From the viewpoint of high stiffness, low thermal expansion, light weight, and wear resistance, however, the silicon nitride type materials are optimum.

[0020] The reflectances of the silicon nitride type materials, however, are so high as to fall in the range of 20 - 30%. A coloring method intended to lower the reflectance remains yet to be developed.

[0021]

[Means to solve the problem] The task of lowering the reflectance of the silicon nitride type sinter mentioned above to a level of not more than 15% by staining the sinter in a black color is fulfilled by preparing a mixed powder comprising 0.2 - 5 wt % of one or more species from among TiC, TiC-TiN solid solution, NbC, ZrC, HfC, and TaC as a coloring agent, 0.1 - 5 wt % of one or more species from among V, Cr, Fe, Co, Ni, Cu, and Hf in the form of a metal or an oxide as a color tone adjusting agent, and the balance substantially of a silicon nitride type material and sintering the mixed powder in an atmosphere of nitrogen under application of no pressure or under the pressure of a gas of not more than 10 kgf/cm² at a temperature in the range of 1600 - 1850°C.

[0022] As a result, it is made possible to obtain a (black) silicon nitride material having a low reflectance of not more than 15% at a low price.

[0023] If the amount of the one or more species selected from among TiC, TiC-TiN solid solution, NbC, ZrC, HfC, and TaC to be added exceeds 5 wt %, the excess will obstruct the sintering of the silicon nitride type, render it impossible to obtain a sinter of an amply dense texture under application

of no pressure, degrade stiffness and wear resistance extremely, and degrade various mechanical properties as well.

[0024] Further, these additives have high thermal expansion coefficients and high specific gravities as compared with
5 those of the silicon nitride type. When they are added in a large amount, therefore, the produced sinter manifests a large thermal expansion coefficient, acquires an increased weight, and entails degradation of the performance.

[0025] If this amount falls short of 0.2 wt %, the shortage
10 will render the staining in a black color insufficient and prevent the reflectance from being lowered.

[0026] Though the amount of this addition varies with the kind of additive, particularly properly it falls in the approximate range of 1 wt % - 3 wt %. The silicon nitride
15 type sinter which retains an amply black color tone and enjoys high density of texture, high stiffness, and low thermal expansion can be produced inexpensively.

[0027] When the blackening additive mentioned above is used alone, the produced sinter possibly suffers from uneven
20 coloration and conspicuous contrast of light and shade. The color tone adjusting agent, therefore, is added for the purpose of stabilizing the black color tone.

[0028] As the color tone adjusting agent, it is proper to add 0.2 - 5 wt % of one species or more species selected from
25 among V, Cr, Fe, Co, Ni, Cu, and Hf in the form of a metal or an oxide.

[0029] The amount of addition in the form of an oxide is optimum in the range of 1 - 5 wt % in the case of V, Cr, and Fe, in the range of 0.5 - 4 wt % in the case of Co, Ni, and
30 Cu, and in the range of 0.2 - 1.5 wt % in the case of Hf. If this amount is unduly small, the effect of adjustment will be small. If the amount is unduly large, the sinter will

possibly form glass of a low melting point and give rise to bubbles.

[0030] The silicon nitride type material means silicon nitride and SIALON. The term "SIALON" embraces α -SIALON and
5 β -SIALON.

[0031] In the case of the silicon nitride, the compounded mixed powder is composed of a silicon nitride powder and a powdered sintering auxiliary.

[0032] The term "sintering auxiliary" as used herein refers
10 to one species or a combination of several species selected from among Y_2O_3 , Al_2O_3 , MgO , SiO_2 , Yr_2O_3 , Er_2O_3 , and Sc_2O_3 .

[0033] The compounded mixed powder in the case of SIALON may comprise a SIALON powder and a sintering auxiliary therefor in some cases and such a silicon nitride powder as is fated
15 to form SIALON after being sintered and some other powder in other cases.

[0034] The particle size of any of the powders used for the raw material is preferred to be not more than 10 μm , particularly not more than 5 μm , on the average from the
20 standpoint of the sintering property.

[0035] If the powder has a larger particle size, the excess will possibly keep the produced sinter from forming a sufficiently dense texture and consequently prevent it from manifesting fully satisfactory stiffness and wear resistance.

[0036] The sintering is carried out in an atmosphere of
25 nitrogen gas under a pressure of not more than 10 kgf/cm^2 in the absence of mechanical pressure. Thus, this sintering is capable of producing a sinter in a varying complicated shape at a low cost as compared with such high pressure sintering
30 as HP and HIP.

[0037] The sintering can be performed at a low temperature in the approximate range of 1600 - 1750°C when the particle

size of the raw material is small and the amount of the sintering auxiliary mentioned above is sufficiently large. The sintering temperature must be in the range of 1700 - 1800°C when the amount of the one species or more species selected from among TiC, TiC-TiN solid solution, ZrC, HfC, and TaC to be added is large and the amount of the sintering auxiliary is small or when the particle size of the raw material powder is large.

[0038] When the sintering is performed at a temperature exceeding 1800°C, it induces decomposition of silicon nitride and SIALON. When the atmospheric pressure (not more than 10 kgf/cm²) is utilized, the sintering can be performed at a temperature elevated up to about 1850°C.

[0039] The sinter produced as described above possesses a color tone of the black type, exhibits such a small integral reflectance as not more than 15% to a visible ray and an ultraviolet light, and enjoys high stiffness, wear resistance, and low thermal expansion.

[0040] Such a low reflectance as falling short of 10% is obtained when the amount of the one species or more species selected from among TiC, TiC-TiN solid solution, ZrC, HfC, and TaC is sufficiently large and the amount of the color tone adjusting agent to be added is moderate.

[0041] Now, this invention will be described specifically below with reference to working examples.

[0042]

[Example 1] In an alumina pot mill, a mixed powder composed of 85.4 parts by weight of silicon nitride powder having an average particle diameter of 0.2 μ m, 4.8 parts by weight of MgO as a sintering auxiliary, 4.8 parts by weight of Al₂O₃, 3 parts by weight of a TiC powder having an average particle diameter of 1 μ m and intended as a coloring agent, and 2 parts

by weight of iron oxide as a color tone adjusting agent was mixed with 3 parts by weight of a resin binder in the presence of water as a solvent for 24 hours.

[0043] The resultant slurry was dried and subjected to size enlargement and then formed under a normal hydrostatic pressure of 2000 kg/cm². The formed piece consequently obtained was subjected to temperature elevation in 1 atmosphere of N₂ gas and sintered at 1750°C for two hours.

[0044] The sinter consequently obtained had a bulk density of 98.0% of the theoretical density, a Young's modulus of elasticity of 3.1×10^4 kgf/mm², and a flexural strength of 85 kgf/mm². The color tone was black and the reflectance was 9.2% at a wavelength in the range of 350 - 800 nm. The thermal expansion coefficient of this sinter at temperatures in the range of 20°C - 100°C was $2.0 \times 10^{-6}/^\circ\text{C}$.

[0045]

[Example 2] In an alumina pot mill, a mixed powder composed of 83.6 parts by weight of a β -SIALON powder having an average particle diameter of 0.7 μm , 4.7 parts by weight of Y₂O₃ as a sintering auxiliary, 5 parts by weight of a Ti(CN) powder having an average particle diameter of 1 μm , and 2 parts by weight of CoO₂ as a color tone adjusting agent was mixed with 3 parts by weight of a resin binder in the presence of water as a solvent for 24 hours.

[0046] The resultant slurry was dried and subjected to size enlargement and then formed under a normal hydrostatic pressure of 2000 kg/cm². The formed piece consequently obtained was subjected to temperature elevation in 1 atmosphere of N₂ gas and sintered at 1850°C for two hours.

[0047] The sinter consequently obtained had a bulk density of 98.5% of the theoretical density, a Young's modulus of elasticity of 3.2×10^4 kgf/mm², and a flexural strength of

78 kgf/mm². The color tone was black brown and the reflectance was 11.5% at a wavelength in the range of 350 - 800 nm. The thermal expansion coefficient of this sinter at temperatures in the range of 20°C - 100°C was $1.8 \times 10^{-6}/^{\circ}\text{C}$.

5 [0048]

[Example 3] In an alumina pot mill, a mixture composed of 97 parts by weight of a powder (silicon nitride powder + Y₂O₃ + AlN) so formulated as to assume a Z value of 2 after being sintered, 2 parts by weight of a NbC powder having an average
10 particle diameter of 0.8 μm and intended as a coloring agent, and 1 part by weight of Hf₂O₃ as a color tone adjusting agent was mixed with 3 parts by weight of a resin binder in the presence of alcohol as a solvent for 24 hours.

[0049] The resultant slurry was dried and subjected to size
15 enlargement and then formed under a normal hydrostatic pressure of 2000 kg/cm². The formed piece consequently obtained was subjected to temperature elevation in 1 atmosphere of N₂ gas and sintered at 1850°C for two hours.

[0050] The sinter consequently obtained had a bulk density
20 of 97.8% of the theoretical density, a Young's modulus of elasticity of 3.0×10^4 kgf/mm², and a flexural strength of 68 kgf/mm². The color tone was black brown and the reflectance was 12.2 % at a wavelength in the range of 350 - 800 nm. The thermal expansion coefficient of this sinter at temperatures
25 in the range of 20°C - 100°C was $1.9 \times 10^{-6}/^{\circ}\text{C}$.

[0051]

[Example 4] In an alumina pot mill, a mixed powder composed of 88.0 parts by weight of an α-SIALON powder having an average particle diameter of 0.3 μm, 5 parts by weight of MgO as a
30 sintering auxiliary, 5 parts by weight of a TaC powder having an average particle diameter of 1 μm and intended as a coloring agent, and 1 part by weight of iron oxide was mixed with 3

parts by weight of a resin binder in the presence of alcohol as a solvent for 24 hours.

[0052] The resultant slurry was dried and subjected to size enlargement and then formed under a normal hydrostatic pressure of 2000 kg/cm². The formed piece consequently obtained was subjected to temperature elevation in 1 atmosphere of N₂ gas and sintered at 1750°C for two hours.

[0053] The sinter consequently obtained had a bulk density of 97.7% of the theoretical density, a Young's modulus of elasticity of 3.2×10^4 kgf/mm², and a flexural strength of 65 kgf/mm². The color tone was black and the reflectance was 10.5% at a wavelength in the range of 350 - 800 nm. The thermal expansion coefficient of this sinter at temperatures in the range of 20°C - 100°C was $2.1 \times 10^{-6}/^\circ\text{C}$.

[0054]

[Example 5] A coloring agent and a color tone adjusting agent were added at varying proportions shown in Table 1 to a silicon nitride mixed powder composed of 91 parts by weight of a silicon nitride powder having an average particle diameter of 0.2 μm, 5 parts by weight of Y₂O₃ as a sintering auxiliary, and 4 parts by weight of Al₂O₃. In an aluminum pot mill, the resultant mixture and 3 parts by weight of a resin binder added thereto were mixed together in water as a solvent.

[0055] The resultant slurries were dried and subjected to size enlargement and then formed under a normal hydrostatic pressure of 2000 kg/cm². The formed pieces consequently obtained were subjected to temperature elevation in 1 atmosphere of N₂ gas and sintered at 1750°C for two hours.

[0056] The sinters consequently obtained had such bulk densities, Young's moduli of elasticity, flexural strengths, reflectances, and thermal expansion coefficients at 20°C - 100°C as shown in Table 1.

[0057]

[Comparative Example] A coloring agent and a color tone adjusting agent were added at varying proportions shown in Table 1 to a silicon nitride mixed powder composed of 91 parts by weight of a silicon nitride powder having an average particle diameter of 0.2 μm , 5 parts by weight of Y_2O_3 as a sintering auxiliary, and 4 parts by weight of Al_2O_3 . In an aluminum pot mill, the resultant mixture and 3 parts by weight of a resin binder added thereto were mixed together in water as a solvent.

[0058] The resultant slurry was dried and subjected to size enlargement and then formed under a normal hydrostatic pressure of 2000 kg/cm^2 . The formed piece consequently obtained was subjected to temperature elevation in 1 atmosphere of N_2 gas and sintered at 1750°C for two hours.

[0059] The sinters consequently obtained had such bulk densities, Young's moduli of elasticity, flexural strengths, reflectances, and thermal expansion coefficients at 20°C - 100°C as shown in Table 2.

[0060]

[Table 1]

Table 1

| Formulation (parts by weight) | | Sintering conditions | Theoretical density ratio (% TD) | Young's modulus of elasticity, \times 10^4 kgf/mm ² | Reflectance (%) |
|----------------------------------|------------------------------------|-------------------------------|--|---|--------------------|
| Coloring agent | Adjusting agent | | | | |
| HfC 5.0 | V 0.5 CoO 2.0 | 1780°C N ₂ latm | 96.5 | 2.9 | 8.7 |
| ZrC 1.0 | CuO 1.0 | 1900°C | 98.9 | 3.2 | 9.6 |
| TaC 3.0 | HfO ₂ 1.0 | N ₂ 10atm | | | |
| TiCN 0.5 | Co 0.5 | 1750°C | 97.2 | 3.0 | 12.3 |
| NbC 0.5 | Fe ₂ O ₃ 2.0 | N ₂ latm | | | |
| TiC 0.2 | Cr ₂ O ₃ 0.5 | 1750°C | 98.2 | 3.0 | 14.5 |
| HfC 0.1 | | N ₂ latm | | | |
| TiCN 0.2 | Fe 1.0 | 1750°C | 98.9 | 3.1 | 12.5 |
| | HfO ₂ 2.0 | N ₂ latm | | | |

[0061] [Table 2]

Table 2 (Comparative Example)

| Formulation (parts by weight) | | Sintering conditions | Theoretical density ratio (% TD) | Young's modulus of elasticity, \times 10^4 kgf/mm ² | Reflectance (%) |
|----------------------------------|---|-------------------------------|--|---|--------------------|
| Coloring agent | Adjusting agent | | | | |
| 0 | 0 | 1780°C N ₂ latm | 98.9 | 3.1 | 29.2 |
| TiC 10.0 | V 0.5 CoO 2.0 | 1780°C N ₂ latm | 87.5 | 2.0 | 11.2 |
| ZrC 0.1 | Co 0.1 | 1750°C N ₂ latm | 98.7 | 3.2 | 22.2 |
| TiCN 0.2 NbC 0.2 | Fe ₂ O ₃ 0.1 | 1750°C N ₂ latm | 98.6 | 3.0 | 17.2 |
| TiC 5.0 HfC 2.0 | Cr ₂ O ₃ 1.0 NiO 1.0 | 1750°C N ₂ latm | 90.2 | 2.3 | 10.3 |
| TiCN 8.0 | Fe 0.1 | 1750°C N ₂ latm | 90.7 | 2.3 | 9.9 |

[0062]

[Effect of the Invention] This invention produces a silicon nitride quality (silicon nitride×SIALON) sinter which is stained in a black color type and consequently allowed to
5 lower the reflectance thereof to a level of not more than 15%. This product can be widely applied to the production of precision parts of optical devices concerned with laser and ultraviolet light which abhor reflection and necessitate high stiffness, low thermal expansion, and wear resistance.

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(54)【発明の名称】 黒色窒化珪素質焼結体とその製造方法

(57)【要約】

【目的】 本発明は、黒色で可視光および紫外線光の積分反射率が15%以下の黒色窒化珪素質焼結体の製造方法に関する。

【構成】 窒化珪素およびサイアロンを黒色系に着色して、可視光および紫外線光の積分反射率を15%以下にする。着色方法としてTiC、TiCN、NbC、ZrC、HfC、TaCの1種または数種を0.2~5重量%含ませ、また色調の調整剤としてV、Cr、Co、Ni、Cu、Hfの1種または数種を金属又は酸化物として0.2~5重量%添加する。

【特許請求の範囲】

【請求項1】 窒化珪素とサイアロン的一种または数種を90%以上含み、可視光および紫外線の積分反射率が15%以下である事を特徴とする黑色窒化珪素質焼結体。

【請求項2】 着色剤としてTiC、TiC—TiN固溶体、NbC、ZrC、HfC、TaCの1種または2種以上を0.2~5wt%含む事を特徴とする請求項1記載の黑色窒化珪素質焼結体。

【請求項3】 色調調整剤としてV、Cr、Fe、Co、Ni、Cu、Hfの1種または数種を金属または酸化物として0.2~5wt%添加する事を特徴とする請求項1記載の黑色窒化珪素質焼結体。

【請求項4】 20~100℃の熱膨張係数が $2.5 \times 10^{-6}/^{\circ}\text{C}$ 以下である事を特徴とする請求項1記載の黑色窒化珪素質焼結体。

【請求項5】 ヤング率が $2.8 \times 10^4 \text{ kgf/mm}^2$ 以上である事を特徴とする請求項1記載の黑色窒化珪素質焼結体。

【請求項6】 焼結温度が1600~1850℃で非加圧または 10 kgf/cm^2 以下の窒素雰囲気加圧下で焼結する事を特徴とする請求項1記載の黑色窒化珪素質焼結体の製造方法。

【発明の詳細な説明】**【0001】**

【産業上の利用分野】本発明は、黑色で可視光および紫外線光の積分反射率が15%以下の黑色窒化珪素質焼結体の製造方法に関する（以後、可視光および紫外線光の積分反射率の事を単に反射率と称する。また積分反射率とは入射光量と全方位に反射した光量の総和との比を意味する）。

【0002】レーザー使用装置や紫外線露光装置等の光関連装置部品の内には光の反射を嫌う部品が多くある。

【0003】それらの部品としては、黒色系色調の反射率の低い材料が求められる。また、それらの部品は精密部品として同時に軽量・高剛性・低熱膨張・耐摩耗性等を求められる場合が多くある。

【0004】これらの部品には本発明の黑色窒化珪素質焼結体が最適で、このような部品に広く適用される。

【0005】以後、窒化珪素とサイアロンを合わせて窒化珪素系と表現する。

【0006】

【従来の技術】従来このような部品としては反射率が低く、軽量と言う条件からアルミニウム合金の表面を黒色アルマイト処理をした部品が良く使用されている。

【0007】しかし、最近これらの部品を使用した機械に要求される精度や寿命が厳しくなり、アルミニウム合金の剛性（弾性率）の低さや、塑性変形しやすさ、高い熱膨張率、耐摩耗性の悪さ等の性質が問題となっている。

【0008】そこで、これらの部品にセラミックスを適用しようとする試みがあるが、黒色（低反射率）・高剛性・軽量・低熱膨張・耐摩耗性を十分に満足する材料はセラミックスでも多くは見当たらない。

【0009】我々が開示している特開平04-50161ではアミルナ焼結体を黒色に着色する技術が開示されている。

【0010】しかし、アルミナの熱膨張率は金属よりは小さいもののまだ十分とはいえず、また耐摩耗性も十分ではない。

【0011】それに対して窒化珪素系の熱膨張率はアルミナの1/3以下で、耐摩耗性も非常に優れている。また比重もアルミナの80%と軽く、より軽量を要求される場合には優っている。

【0012】しかし、窒化珪素系焼結体は一般には淡灰色から灰色で、その反射率は20~35%と大きい。

【0013】この窒化珪素系材料に着色する技術としてはTiNを30%程度入れて金色系に着色する技術があるが金色系では反射率はあまり下らない。

【0014】また、その他の着色技術については、特開昭62-248773と特開平01-192766に、黑色窒化珪素質焼結体について開示されている。

【0015】前者はSc、Yb、Er、Ho、Dyの化合物を添加する事、後者はCoまたはFeを含む有機金属化合物を添加する事により黒色化しており、本発明とは異なる。

【0016】特開昭62-235260には窒化珪素にTiN、TiC、Ti(CN)の1種以上を5~40wt%添加しHIP焼結する焼結体について開示されているが、これらの添加物をこのように多量に添加すると比重が重くなり、また焼結性が阻害されてHIP・HP等の圧力焼成が必要となり焼成費用により高価な焼結体になってしまう。

【0017】また、その色や反射率については触れられていない。

【0018】

【発明が解決しようとする課題】このように金属材料では高剛性・低熱膨張・軽量・耐摩耗を同時に満足する材料は見当たらない。

【0019】また、セラミックスについては反射率が15%以下という材料は種々あるが、高剛性・低熱膨張・軽量・耐摩耗の観点からは窒化珪素系の材料が最適である。

【0020】しかし、窒化珪素系の材料の反射率は20~30%と高く、また反射率を下げるための着色方法は従来得られていない。

【0021】

【課題を解決するための手段】上記の窒化珪素系焼結体を黒色化して反射率を15%以下にするという課題は、着色剤としてTiC、TiC—TiN固溶体、NbC、

ZrC、HfC、TaCの1種または2種以上を0.2～5wt%含み、また色調調整剤としてV、Cr、Fe、Co、Ni、Cu、Hfの1種または2種以上を金属または酸化物として0.1～5wt%含み、残部が実質的に窒化珪素系材料よりなる混合粉体を窒素雰囲気の下で非加圧または10kgf/cm²以下のガス圧条件で1600～1850℃の温度範囲で焼結する事により解決される。

【0022】このようにすれば反射率が15%以下の低い(黒色化)窒化珪素系材料が低価格でえられる。

【0023】TiC、TiC—TiN固溶体、NbC、ZrC、HfC、TaCの1種または2種以上の添加量は5wt%以上では窒化珪素系の焼結を阻害し、非加圧では十分緻密な焼結体を得られず、剛性や耐摩耗性を極端に低下させると共に各種の機械的性質が低下する。

【0024】また、これらの添加物は窒化珪素系の物と比較して熱膨張率が高く、また比重が高いため多量に添加すると熱膨張率が大きく、重量が重くなり性能が低下する。

【0025】また0.2wt%以下では黒色の着色が不十分となり反射率は低下しない。

【0026】この添加量は添加物により異なるが、特に1wt%～3wt%程度が好ましく十分な黒色の色調を保有し、緻密で高剛性・低熱膨張の窒化珪素系焼結体が安価に製造できる。

【0027】色調調整剤とは上記の黒色化添加剤のみでは色むらや濃淡が発生する場合があります、黒色色調の安定化させるために添加するものである。

【0028】これらの色調調整剤はV、Cr、Fe、Co、Ni、Cu、Hfの1種または2種以上を金属または酸化物として0.2～5wt%添加する事が好ましい。

【0029】添加量は酸化物としてV、Cr、Feの場合1～5wt%、Co、Ni、Cuの場合0.5～4wt%、Hfの場合0.2～1.5wt%が最適であり少ないと調整効果が少なく、あまり多いと低融点のガラス等を生成して発泡する場合がある。

【0030】窒化珪素系材料は窒化珪素とサイアロンを意味しており、サイアロンとは α -サイアロンと β -サイアロンを含む。

【0031】窒化珪素の場合の配合混合粉末は窒化珪素粉末とその焼結助剤粉末よりなる。

【0032】ここで言う焼結助剤としてはY₂O₃、Al₂O₃、MgO、SiO₂、Yr₂O₃、Er₂O₃、Sc₂O₃等の1種または数種の組合せを言う。

【0033】一方サイアロンの場合の配合混合粉末はサイアロン粉末とその焼結助剤よりなる場合と焼結後にサイアロンとなるような窒化珪素粉末とその他の粉末よりなる場合がある。

【0034】原料に使用する粉体の粒度はその焼結性の

面から平均粒径10 μ m以下である事が好ましく、特に5 μ m以下であることが望ましい。

【0035】それ以上の粒度の粉体では十分緻密な焼結体は得られず、そのため充分に高い剛性・耐摩耗性が得られない場合がある。

【0036】焼結は窒素雰囲気中で行なわれ、機械的圧力はなく、雰囲気圧力は10kgf/cm²以下で実施されるため、HPやHIP等の高圧焼結に比較して安価に各種の複雑形状品が焼成できる。

【0037】焼結温度は原料の粒度が小さく、上記焼結助剤が十分多い場合には1600～1750℃程度の低い温度で焼結可能であるが、TiC、TiC—TiN固溶体、NbC、ZrC、HfC、TaCの1種または2種以上の添加量が多く、焼結助剤が少ない場合、または原料粉体の粒度が大きい場合には1700～1800℃が必要である。

【0038】1800℃以上では窒化珪素・サイアロンの分解が発生するが、雰囲気加圧(10kgf/cm²以下)を利用した場合には1850℃程度まで高温での焼結が可能である。

【0039】このようにして製造された焼結体は黒色系の色調をもち、その可視光および紫外線の積分反射率は15%以下と小さく、また高い剛性と耐摩耗性、低熱膨張性を有する。

【0040】TiC、TiC—TiN固溶体、NbC、ZrC、HfC、TaCの1種または2種以上の添加量が十分多く、色調添加剤が適度に添加された場合には10%以下の低反射率が得られる。

【0041】以下、実施例によって本発明を具体的に説明する。

【0042】

【実施例1】平均粒径0.2 μ mの窒化珪素粉末85.4重量部に焼結助剤としてMgO4.8重量部、Al₂O₃4.8重量部、着色剤として平均粒径1 μ mのTiC粉末3重量部、色調調整剤として酸化鉄2重量部よりなる混合粉体に樹脂バインダー3重量部を加え、水を溶媒としてアルミナボットミル中で24時間混合した。

【0043】このスラリーを乾燥造粒し、静水圧2000kgf/cm²で成形した。得られた成形体をN₂ガス1atm中で昇温し、1750℃で2時間焼結した。

【0044】得られた焼結体の嵩密度は理論密度の98.0%、ヤング率は3.1 $\times 10^4$ kgf/mm²、曲げ強度は85kgf/mm²で色調は黒色で反射率は波長350～800nmの間で9.2%であった。また20℃～100℃の熱膨張係数は2.0 $\times 10^{-6}$ /℃であった。

【0045】

【実施例2】平均粒径0.7 μ mの β -サイアロン粉末83.6重量部に焼結助剤としてY₂O₃4.7重量部、Al₂O₃4.7重量部、着色剤として平均粒径1 μ mの

Ti(CN)粉末5重量部、色調調整剤としてCoO₂重量部よりなる混合粉末に樹脂バインダー3重量部を加え、水を溶媒としてアルミナボットミル中で24時間混合した。

【0046】このスラリーを乾燥造粒し、静水圧2000kg/cm²で成形した。得られた成形体をN₂ガス10atm中で昇温し、1850℃で2時間焼結した。

【0047】得られた焼結体の嵩密度は理論密度の98.5%、ヤング率は 3.2×10^4 kgf/mm²、曲げ強度は78kgf/mm²で色調は黒茶色で反射率は波長350~800nmの間で11.5%であった。また20℃~100℃の熱膨張係数は 1.8×10^{-6} /℃であった。

【0048】

【実施例3】焼結後Z値が2になるように調合された粉末(窒化珪素粉末+Y₂O₃+Al₂O₃+AlN)97重量部に、着色剤として平均粒径0.8μmのNbC粉末2重量部、色調調整剤としてHf₂O₃1重量部を混合し、樹脂バインダー3重量部を加え、アルコールを溶媒としてアルミナボットミル中で24時間混合した。

【0049】このスラリーを乾燥造粒し、静水圧2000kg/cm²で成形した。得られた成形体をN₂ガス10atm中で昇温し、1850℃で2時間焼結した。

【0050】得られた焼結体の嵩密度は理論密度の97.8%、ヤング率は 3.0×10^4 kgf/mm²、曲げ強度は68kgf/mm²で色調は黒褐色で反射率は波長350~800nmの間で12.2%であった。また20℃~100℃の熱膨張係数は 1.9×10^{-6} /℃であった。

【0051】

【実施例4】平均粒径0.3μmのα-サイアロン粉末88.0重量部に焼結助剤として、MgO5重量部、着色剤として平均粒径1μmのTaC粉末5重量部、色調調整剤としてNiO1重量部、酸化鉄1重量部よりなる混合粉末に樹脂バインダー3重量部を加え、アルコールを溶媒としてアルミナボットミル中で24時間混合した。

【0052】このスラリーを乾燥造粒し、静水圧2000kg/cm²で成形した。得られた成形体をN₂ガス10atm中で昇温し、1750℃で2時間焼結した。

【0053】得られた焼結体の嵩密度は理論密度の97.7%、ヤング率は 3.2×10^4 kgf/mm²、曲げ強度は65kgf/mm²で色調は黒色で反射率は波長350~800nmの間で10.5%であった。また20℃~100℃の熱膨張係数は 2.1×10^{-6} /℃であった。

【0054】

【実施例5】平均粒径0.2μmの窒化珪素粉末91重量部に焼結助剤としてY₂O₃5重量部、Al₂O₃4重量部よりなる窒化珪素混合粉末に対して着色剤や色調調整剤を第1表の割合で混合し、樹脂バインダー3重量部を加え、水を溶媒としてアルミナボットミル中で24時間混合した。

【0055】このスラリーを乾燥造粒し、静水圧2000kg/cm²で成形した。得られた成形体をN₂ガス10atm中で昇温し、1750℃で2時間焼結した。

【0056】得られた焼結体の嵩密度・ヤング率・曲げ強度・反射率・20℃~100℃の熱膨張係数を第1表にしめた。

【0057】

【比較例】平均粒径0.2μmの窒化珪素粉末91重量部に焼結助剤としてY₂O₃5重量部、Al₂O₃4重量部よりなる窒化珪素混合粉末に対して着色剤や色調調整剤を第1表の割合で混合し、樹脂バインダー3重量部を加え、水を溶媒としてアルミナボットミル中で24時間混合した。

【0058】このスラリーを乾燥造粒し、静水圧2000kg/cm²で成形した。得られた成形体をN₂ガス10atm中で昇温し、1750℃で2時間焼結した。

【0059】得られた焼結体の嵩密度・ヤング率・曲げ強度・反射率・20℃~100℃の熱膨張係数を第2表にしめた。

【0060】

【表1】

第1表

| 配合(重量部) | | 焼成条件 | 理論密度比 (%TD) | ヤング率 $\times 10^4$ kgf/mm ² | 反射率 (%) |
|---------------------|--|--------------------------------|----------------|---|------------|
| 着色剤 | 調整剤 | | | | |
| HfC 5.0 | V 0.5 CoO 2.0 | 1780°C N ₂ 1atm | 96.5 | 2.9 | 8.7 |
| ZrC 1.0 TaC 3.0 | CuO 1.0 HfO ₂ 1.0 | 1900°C N ₂ 10atm | 98.9 | 3.2 | 9.6 |
| TiCN 0.5 NbC 0.5 | Co 0.5 Fe ₂ O ₃ 2.0 | 1750°C N ₂ 1atm | 97.2 | 3.0 | 12.3 |
| TiC 0.2 HfC 0.1 | Cr ₂ O ₃ 0.5 | " | 98.2 | " | 14.5 |
| TiCN 0.2 | Fe 1.0 HfO ₂ 2.0 | " | 98.9 | 3.1 | 12.5 |

【表2】

【0061】

第 2 表 (比較例)

| 配合 (重量部) | | 焼成条件 | 理論密度比 (%TD) | ヤング率 $\times 10^4$ kgf/mm ² | 反射率 (%) |
|---------------------|---|--------------------------------|----------------|---|-------------|
| 着色剤 | 調整剤 | | | | |
| 0 | 0 | 1780°C N ₂ 1 atm | 98.9 | 3.1 | 29.2 |
| TiC 10.0 | V 0.5 CoO 2.0 | " | 87.5 | 2.0 | 11.2 |
| ZrC 0.1 | Co 0.1 | 1750°C N ₂ 1 atm | 98.7 | 3.2 | 22.2 |
| TiCN 0.2 NbC 0.2 | Fe ₂ O ₃ 0.1 | " | 98.6 | 3.0 | 17.2 色むら |
| TiC 5.0 HfC 2.0 | Cr ₂ O ₃ 1.0 NiO 1.0 | " | 90.2 | 2.3 | 10.3 |
| TiCN 8.0 | Fe 0.1 | " | 90.7 | " | 9.9 |

【0062】

【発明の効果】本発明は、窒化珪素質（窒化珪素・サイアロン）焼結体に黒色系の着色をし、15%以下の反射

率にして、反射を嫌いまた高剛性・低熱膨張・耐摩耗性を必要とするレーザー・紫外線等の光装置関連の精密部品の製造に広く応用可能である。